

PATENT ABSTRACTS OF JAPAN

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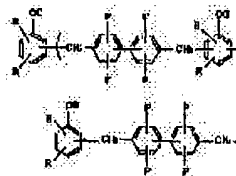
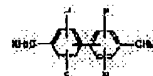
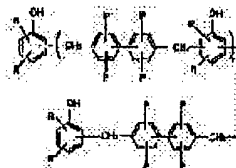
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(54) NOVOLAK TYPE RESIN, EPOXY RESIN, EPOXY RESIN COMPOSITION AND ITS CURED MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject resin capable of providing a curd material excellent in water resistance and mechanical strength, useful as a molding material, a casting material, a coating material, an adhesive, having a specific molecular structure and a molecular weight distribution.

SOLUTION: This novolak resin is shown by formula I ((n) is an average value and is a value of 0-10; P and Q are each H, a halogen, a 1-8C alkyl or an aryl) and has <math>\geq 70\% area ratio of a rate in which (n) is 0 in formula I in GPC(gel permeation chromatography) analysis. The compound of formula I is obtained, for example, by condensing a compound of formula II (X is a halogen, hydroxyl group or a lower alkoxy) with a phenol in the presence of an acid catalyst. The compound of formula I is reacted with an epihalohydrin in the presence of an alkali metal hydroxide to give an epoxy resin of formula III (G is glycidyl). The epoxy resin has <math>\geq 70\% area ratio of a rate in which (n) is 0 in formula II is GPC analysis.



LEGAL STATUS

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DERWENT-WEEK: 199751

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TITLE: Novolak resins for use in epoxy
resins for e.g. moulding
and casting materials - have good
working efficiency and
give cured products with good water
resistance, toughness
and mechanical strength

PATENT-ASSIGNEE: NIPPON KAYAKU KK[NIPK]

PRIORITY-DATA: 1996JP-0099581 (March 29, 1996)

PATENT-FAMILY:

PUB-NO	PAGES	PUB-DATE	MAIN-IPC
JP 09268219 A		October 14, 1997	N/A
008	C08G 059/06		

APPLICATION-DATA:

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1996JP-0099581	March 29, 1996	

INT-CL (IPC): C08G059/06, C08G059/18 , C08G059/20

ABSTRACTED-PUB-NO: JP 09268219A

BASIC-ABSTRACT:

Novolak resins of formula (1) contain (1) in which n = 0 in amounts of below 70% in area ratio (by GPC analysis). In (1), n = average value of 0-10; and P, R = H, halogen, 1-8 C alkyl or aryl.

Also claimed are epoxy resins of formula (2) containing (1) in which n = 0 in amounts of below 70 % in area ratio (by GPC analysis). In

(2), G = glycidyl.

USE - The novolak resins and epoxy resins are used for moulding materials, casting materials, lamination materials, paints, adhesives and paints. Cured products obtained by curing epoxy resin compositions containing (a) epoxy resins and (b) the novolak resins (claimed), or containing (c) the epoxy resins and (d) hardeners (claimed), or containing (c) and (b) (claimed), or the epoxy resin compositions containing further (e) curing accelerators (claimed) and optionally (f) inorganic fillers (claimed) (the cured products are also claimed) are used for electric and electronic materials e.g. sealing materials, laminated sheets, insulating materials; moulding materials, adhesives, composite materials, paints.

ADVANTAGE - The novolak resins and epoxy resins have good working efficiency and provide cured products having good water resistance, toughness and mechanical strength.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: NOVOLAK RESIN EPOXY RESIN MOULD CAST MATERIAL
WORK EFFICIENCY CURE
PRODUCT WATER RESISTANCE TOUGH MECHANICAL
STRENGTH

DERWENT-CLASS: A21 G02 G03

CPI-CODES: A05-A01B1; A05-C01A; A08-D; A08-R01; G02-A02G;
G03-B02E2; G04-B02;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0760U

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Polymer Index [1.1]

018 ; H0022 H0011 ; G1069 G1025 G0997 D01 F28 F26 D11
D10 D19 D18

D18*R D32 D33 D34 D35 D76 D50 D69 D93 D94 D95 7A*R ;
G1105*R G1092

AN 1997:678686 CAPLUS
 DN 127:279003
 ED Entered STN: 25 Oct 1997
 TI Novolak resin, epoxy resin, epoxy composition, and their cured products
 with good water resistance and toughness
 IN Akatsuka, Yasumasa; Shimamura, Yoshiro; Hasegawa, Ryoichi
 PA Nippon Kayaku Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 8 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08G059-06
 ICS C08G059-18; C08G059-20
 CC 37-3 (Plastics Manufacture and Processing)
 Section cross-reference(s): 35

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PI	JP 09268219	A2	19971014	JP 1996-99581	19960329
PRAI	JP 1996-99581		19960329		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 09268219	ICM	C08G059-06
	ICS	C08G059-18; C08G059-20

AB Title compn. contains (A) a novel novolak resin prepd. by condensation of
 biphenyldimethanol derivs. and phenols and/or (B) a glycidyl ether of the
 above novolak, wherein low-mol.-wt. mols. in both resins account for
 .ltoreq.70% area ratio in GPC chart. Thus,
 4,4'-biphenyldimethanol-phenol
 copolymer 73, 4,4'-biphenyldimethanol-phenol copolymer glycidyl ether 100
 and tri-Ph phosphine 1 part were mixed, molded and cured to give a
 product

ST epoxy novolak resin water resistance; impact resistance curable novolak
 epoxy resin; biphenylmethanol phenol novolak crosslinking agent; glycidyl
 ether biphenylmethanol phenol novolak epoxy

IT Water-resistant materials
 Water-resistant materials
 (impact-resistant; novel novolak and epoxy resin with good water
 resistance and toughness)

IT Water-resistant materials
 (novel novolak and epoxy resin with good water resistance and
 toughness)

IT Phenolic resins, preparation
 RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP
 (Preparation); USES (Uses)
 (novolak, phenol-biphenyldimethanol condensate, crosslinking agents;
 novel novolak and epoxy resin with good water resistance and
 toughness)

IT Crosslinking agents
 (phenol-biphenyldimethanol condensate; novel novolak and epoxy resin
 with good water resistance and toughness)

IT Epoxy resins, preparation
 RL: IMF (Industrial manufacture); PRP (Properties); PREP (Preparation)
 (phenolic, novolak; novel novolak and epoxy resin with good water
 resistance and toughness)

IT Impact-resistant materials
 Impact-resistant materials

(water-resistant; novel novolak and epoxy resin with good water resistance and toughness)

IT **187344-76-9P**, 4,4'-Biphenyldimethanol-phenol copolymer
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)
(crosslinking agent; novel novolak and epoxy resin with good water resistance and toughness)

IT **187344-76-9DP**, 4,4'-Biphenyldimethanol-phenol copolymer, glycidyl ethers
RL: IMF (Industrial manufacture); POF (Polymer in formulation); PRP (Properties); PREP (Preparation); USES (Uses)
(novel novolak and epoxy resin with good water resistance and toughness)

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the novolak mold resin, epoxy resin, and epoxy resin constituent which give the hardened material which is excellent in a water resisting property and a mechanical strength.

[0002]

[Description of the Prior Art] By making it harden with various curing agents, an epoxy resin serves as a hardened material which was [electrical property / a mechanical property, a water resisting property, chemical resistance, thermal resistance,] generally excellent, and is used for broad fields, such as adhesives, a coating, a laminate, a molding material, and a casting ingredient. There is a liquefied and solid bisphenol A mold epoxy resin which epichlorohydrin is made to react to bisphenol A as an epoxy resin currently used industrial most conventionally, and is obtained. In addition, the fire-resistant solid epoxy resin which tetra-bromine bisphenol A is made to react to the liquefied bisphenol A mold epoxy resin, and is obtained is industrially used as a general-purpose epoxy resin.

[0003]

[Problem(s) to be Solved by the Invention] However, although the toughness of the hardened material with which it is hardened and molecular weight is obtained as a general-purpose epoxy resin which was described above becomes large increases, the fault that thermal resistance falls has it. Moreover, although thermal resistance becomes high in the hardened material obtained when polyfunctional epoxy resins, such as a cresol novolak epoxy resin, are mixed, in order to compensate a heat-resistant fall, toughness falls and water absorption has the fault of becoming high. The water resisting property and mechanical strength (toughness) which are required of the electrical insulation material used for these in connection with **** better *****, such as the latest electronic industry, on the other hand are still severer, and it waits eagerly for the appearance of the curing agent and an epoxy resin excellent in these properties.

[0004] The novolak mold resin (curing agent) and the epoxy resin which had a biphenyl-phenol frame in JP,5-117350,A as an example of the epoxy resin which fills such a demand, and its curing agent are illustrated. However, if the rate of the molecule of the

low molecular weight contained in resin is high in the case of such novolak mold resin of structure, the obtained resin will tend to serve as a high crystal of the melting point. When novolak mold resin becomes the high crystal of the melting point, there is a problem that the ejection from an after [purification] reactor becomes difficult. Moreover, in order to use it as a curing agent of an epoxy resin, the need which must make temperature at the time of kneading very high arises, and there is a possibility of causing trouble to workability.

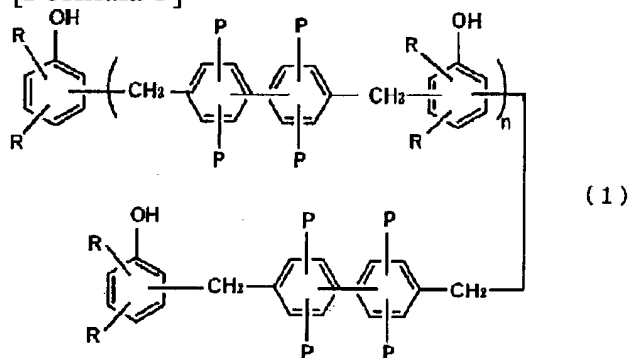
[0005]

[Means for Solving the Problem] In view of the actual condition which carried out this invention person claudication, the hardened material which is excellent in a water resisting property and mechanical strength was given, and as a result of inquiring wholeheartedly in quest of the curing agent and epoxy resin which were moreover excellent in workability, it finds out that it is that with which the novolak mold resin and the epoxy resin which have the specific molecular structure and a specific molecular weight distribution fill the aforementioned property, and came to complete this invention.

[0006] That is, this invention is a formula (1).

[0007]

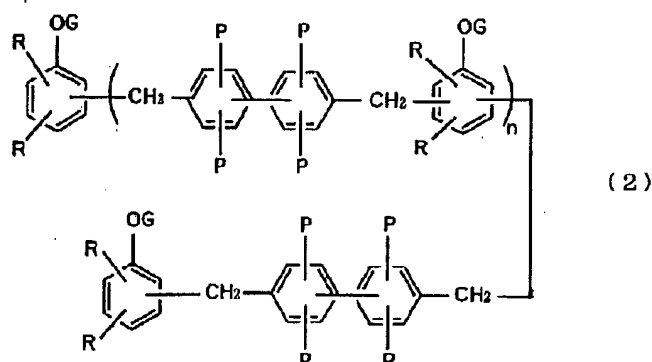
[Formula 3]



[0008] (Among a formula (1), \bar{n} shows the average and takes the value of 0-10.) \bar{P} and \bar{R} express either a hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-8 or an aryl group, respectively, and even if each P and R are mutually the same, they may differ. The novolak mold resin, (2) types (2) whose percentage of the thing [in / on GPC (gel permeation chromatography) analysis and / a formula (1)] of $n=0$ it is novolak mold resin expressed and is 70% or less in surface ratio

[0009]

[Formula 4]



[0010] (n, P, and R express the semantics same in a formula (1) among a formula (2).) Moreover, G expresses a glycidyl group. Epoxy resin whose percentage of the thing [in / on GPC analysis and / a formula (2)] of n= 0 it is the epoxy resin expressed and is 70% or less in surface ratio.

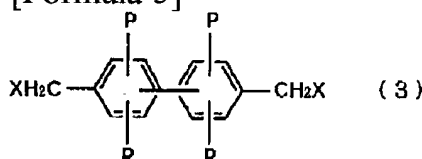
[0011] (3) The epoxy resin constituent which comes to contain novolak mold resin given in (a) epoxy resin (b) above-mentioned (1), (4) The epoxy resin constituent which comes to contain an epoxy resin (b) curing agent given in (a) above-mentioned (2), (5) The epoxy resin constituent which comes to contain novolak mold resin [given in (a) above-mentioned (2)] given in epoxy resin (b) above-mentioned (1), (6) The above (3) containing a hardening accelerator, (4), or an epoxy resin constituent given in any 1 term of (5), (7) The hardened material which comes to harden the epoxy resin constituent of a publication in any 1 term of the above (3) containing an inorganic filler, (4), (5) or an epoxy resin constituent given in any 1 term of (6), (8) above (3), (4), (5), (6), or (7) is offered.

[0012]

[Embodiment of the Invention] The compound expressed with a formula (1) is a formula (3).

[0013]

[Formula 5]



[0014] (X expresses a halogen atom, a hydroxyl group, and a lower alkoxy group among a formula.) P expresses the semantics same in a formula (1).

[0015] It can obtain by coming out and carrying out the condensation reaction of the compound and phenols which are expressed under existence of an acid catalyst.

[0016] The compound expressed with a formula (2) can be obtained by performing the reaction of the compound and epihalohydrin which are expressed with a formula (1) under existence of an alkali-metal hydroxide.

[0017] In a formula (3), a chlorine atom and a bromine atom are mentioned as a halogen atom again as an example in which a methoxy group, an ethoxy radical, etc. are desirable respectively as a lower alkoxy group.

[0018] As an example of the phenols which can be used in order to obtain the compound of a formula (1) here A phenol, cresol, ethylphenol, n-propyl phenol, An isobutyl phenol, t-butylphenol, octyl phenol, Various o-, such as nonyl phenol, a xylenol, a methylbutyl phenol, and G t-butylphenol, m-, p-isomer or a cyclopentyl phenol, a cyclohexyl phenol, Halogenation phenols, such as permutation phenols, such as cycloalkyl phenols, such as cyclohexyl cresol, or phenylphenol, or a mono-BUROMO phenol, and dibromophenol, are mentioned. These phenols may use only one kind and may use it combining two or more kinds.

[0019] one mol of compounds by which the amount of the phenols used is expressed with a formula (3) when performing the above-mentioned condensation reaction -- receiving -- usually -- 1.2-8-mol 1.1-10 mols are 1.2-5 mols especially preferably preferably. When there is much amount of the phenols used, in case residual phenols are distilled off, the obtained condensate serves as a high-melting crystal, and there is a possibility that it may become impossible to take out from a concentrator. In order to prevent the problem of this crystallization, the area rate to a gross area when the rate of the thing of $n=0$ in a formula (1) measures molecular weight distribution using GPC is 70% or less of thing, and the molecular weight distribution of an effective condensate are 65% or less of things preferably.

[0020] An acid catalyst is used in the above-mentioned condensation reaction. Although various things can be used as an acid catalyst, Lewis acid, such as inorganic [, such as a hydrochloric acid, a sulfuric acid, p-toluenesulfonic acid, and oxalic acid] or an organic acid, 3 fluoridation boron, anhydrous salt-sized aluminum, and a zinc chloride, is desirable, and especially p-toluenesulfonic acid, a sulfuric acid, and a hydrochloric acid are desirable. 0.1- of a compound usually expressed with a formula (3) although especially the amount of these acid catalysts used is not limited -- it uses 30% of the weight.

[0021] The above-mentioned condensation reaction can be performed under a non-solvent or existence of an organic solvent. As an example of the organic solvent which can be used, methyl cellosolve, ethylcellosolve, toluene, a xylene, methyl isobutyl ketone, etc. are mentioned. The amount of the organic solvent used is usually 100 - 250 % of the weight preferably 50 to 300% of the weight to the AUW of the prepared raw material. Reaction temperature is 40-180 degrees C, and reaction time is usually 1 - 10 hours. These solvents are independent, or they can mix and use some kinds. Moreover, it is desirable to use water or alcohols generated during a reaction out of a system, and to distill off a fractionating column etc., when reacting promptly.

[0022] the pH value of after reaction termination and a penetrant remover -- 3-7 -- rinsing processing is performed until it is preferably set to 5-7. When performing rinsing processing, various alkalis, such as organic amines, such as diethylenetriamine, triethylenetetramine, an aniline, and a phenylenediamine, etc. may be used for alkaline earth metal hydroxides, such as alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, a calcium hydroxide, and a magnesium hydroxide, ammonia, and a sodium-dihydrogenphosphate pan as a neutralizer as occasion demands. Moreover, what is necessary is just to perform rinsing processing according to a conventional method. For example, the water which dissolved the above-mentioned neutralizer is added into a

reaction mixture, and liquid separation extract operation is repeated.

[0023] After performing neutralization processing, a solvent and an unreacted object can be distilled off under heating under reduced pressure, a product can be condensed, and the novolak mold resin of this invention expressed with a formula (1) can be obtained.

[0024] An approach well-known as an approach of obtaining the epoxy resin of this invention from the compound expressed with a formula (1) is employable. For example, the epoxy resin of this invention can be obtained by making it react at the temperature of 20-120 degrees C for 1 to 10 hours, adding alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, into the compound expressed with the formula (1) obtained above, and the dissolution mixture of epihalohydrin, such as superfluous epichlorohydrin and EPIBUROMUHI drine compounds, or adding into them.

[0025] The approach of making distill water and epihalohydrin continuously under the bottom of reduced pressure or ordinary pressure, while an alkali-metal hydroxide may use the water solution in the reaction which obtains the epoxy resin of this invention and adding the water solution of this alkali-metal hydroxide in the system of reaction continuously in that case, and separating liquids further, removing water, and returning continuously [epihalohydrin] in the system of reaction may be used.

[0026] Moreover, the approach of adding quarternary ammonium salt, such as tetramethyl ammoniumchloride, a tetramethylammonium star's picture, and trimethyl benzyl ammoniumchloride, as a catalyst into the compound and the dissolution mixture of epihalohydrin which are expressed with a formula (1), adding the solid-state or water solution of an alkali-metal hydroxide to the halohydrin etherification object of the compound of the formula (1) which is made to react for 1 to 5 hours, and is obtained at 50-150 degrees C, making react at 20-120 degrees C for 1 to 10 hours, and carrying out a dehydrohalogenation (ring closure) may be used. In this case, the amounts of the quarternary ammonium salt used are usually 1-10g to one hydroxyl group in the compound of a formula (1), and are 2-8g preferably.

[0027] 1-20 mols of amounts of the epihalohydrin used in these reactions are usually 2-10 mols preferably to 1Eq of hydroxyl groups of the compound expressed with a formula (1). The 0.8-1.5 mols of the amount of the alkali-metal hydroxide used are usually 0.9-1.1 mols preferably to 1Eq of hydroxyl groups of the compound expressed with a formula (1). Furthermore, in order to advance a reaction smoothly, it is desirable to react by adding aprotic polar solvents, such as a dimethyl sulfone besides alcohols, such as a methanol and ethanol, and dimethyl sulfoxide, etc.

[0028] When using alcohols, the amount used is usually 4 - 15 % of the weight preferably two to 20% of the weight to the amount of epihalohydrin. Moreover, when using an aprotic polar solvent, it is usually 10 - 90 % of the weight preferably five to 100% of the weight to the amount of epihalohydrin.

[0029] Epihalohydrin, a solvent, etc. are removed without rinsing after rinsing the reactant of these epoxidation reactions by scale loss pressing down, 110-250 degrees C, and 10 or less mmHg of pressures. Furthermore, in order to consider as an epoxy resin with few hydrolysis nature halogens, the obtained epoxy resin can be dissolved in solvents, such as toluene and methyl isobutyl ketone, the water solution of alkali-metal hydroxides, such as

a sodium hydroxide and a potassium hydroxide, can be added, it can react further, and a ring closure can also be made into a positive thing. In this case, the 0.01-0.3 mols of the amount of the alkali-metal hydroxide used are usually 0.05-0.2 mols preferably to 1Eq of hydroxyl groups of the compound of the formula (1) used for epoxidation. Reaction temperature is 50-120 degrees C, and reaction time is usually 0.5 - 2 hours.

[0030] Filtration, rinsing, etc. remove the generated salt after reaction termination, and the epoxy resin of this invention is further obtained by distilling off solvents, such as scale loss pressing-down toluene and methyl isobutyl ketone.

[0031] Hereafter, the epoxy resin constituent of this invention is explained. In an epoxy resin constituent the above (3), (5), (6), and given in (7), the novolak mold resin of this invention can act as a curing agent of an epoxy resin, and can use together the novolak mold resin of this invention with other independent or curing agents in this case. When using together, the rate of occupying in the full hard-ized agent of the novolak mold resin of this invention has 30 desirable % of the weight or more, and especially its 40 % of the weight or more is desirable.

[0032] As other curing agents used together with the novolak mold resin of this invention, an amine system compound, an acid-anhydride system compound, an amide system compound, a phenol system compound, etc. are mentioned, for example. As an example of the curing agent which can be used, diamino diphenylmethane, diethylenetriamine, Triethylenetetramine, diaminodiphenyl sulfone, isophorone diamine, A dicyandiamide, the polyamide resin compounded from the dimer and ethylenediamine of a linolenic acid, Phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, a maleic anhydride, Tetrahydro phthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, an anhydrous methyl NAJIKKU acid, Although hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, phenol novolaks and these denaturation objects, an imidazole, a BF₃-amine complex, a guanidine derivative, etc. are mentioned If well-known as a curing agent of an epoxy resin, it will not be limited to especially these. These curing agents may be used independently and may be used together two or more sorts.

[0033] The epoxy resin of this invention can be used in an epoxy resin constituent the above (4), (5), (6), and given in (7), using it together with other independent or epoxy resins. When using together, the rate of occupying in all the epoxy resins of the epoxy resin of this invention has 30 desirable % of the weight or more, and especially its 40 % of the weight or more is desirable.

[0034] Although a novolak mold epoxy resin, the bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, a biphenyl mold epoxy resin, etc. are mentioned as an example of other epoxy resins in which it is used together with the epoxy resin of this invention, and deals, these may be used independently and may be used together two or more sorts.

[0035] In the epoxy resin constituent of the above (3), (6), and (7), when using the novolak mold resin of this invention as a curing agent, as an epoxy resin, other aforementioned epoxy resins and the epoxy resin of this invention can be used.

[0036] Moreover, in the epoxy resin constituent of the above (4), (6), and (7), when using the epoxy resin of this invention as an epoxy resin, as a curing agent, other aforementioned

curing agents and the novolak mold resin of this invention can be used.

[0037] In the epoxy resin constituent of this invention, the amount of the curing agent used has desirable 0.7-1.2Eq to 1Eq of epoxy groups of an epoxy resin. When not fulfilling 0.7Eq to 1Eq of epoxy groups, or when exceeding 1.2Eq, all have a possibility that hardening may become imperfect and good hardened material nature may not be obtained.

[0038] Moreover, in case the above-mentioned curing agent is used, even if it uses a hardening accelerator together, it does not interfere. As an example of the hardening accelerator which can be used, metallic compounds, such as phosphines, such as imidazole derivatives, such as 2-methylimidazole, 2-ethyl imidazole, and 2-ethyl-4-methylimidazole, 2-(dimethyl aminomethyl) phenol, 1, tertiary amine of 8-diazabicyclo (5, 4, 0) undecene-7 grade, and triphenyl phosphine, and octylic acid tin, etc. are mentioned. As for a hardening accelerator, the 0.1 - 5.0 weight section is used if needed to the epoxy resin 100 weight section.

[0039] The epoxy resin constituent of this invention contains an inorganic filler as occasion demands. A silica, an alumina, talc, etc. are mentioned as an example of the inorganic filler which can be used. The amount to which an inorganic filler occupies 0 - 90 % of the weight in the epoxy resin constituent of this invention is used if needed. Furthermore to the epoxy resin constituent of this invention, various compounding agents, such as release agents, such as a silane coupling agent, stearin acid, a palmitic acid, zinc stearate, and calcium stearate, and a pigment, can be added.

[0040] The epoxy resin constituent of this invention is obtained by predetermined coming out of each component comparatively, and mixing uniformly. The epoxy resin constituent of this invention can be easily used as the hardened material by the approach learned conventionally and the same approach. For example, it fully mixes and the epoxy resin constituent of this invention is obtained until it becomes homogeneity at a hardening accelerator and an inorganic filler list using an extruder, a kneader, a roll, etc. if needed about various compounding agents according to the epoxy resin of this invention, a curing agent, and the need, the epoxy resin constituent can be fabricated using after [melting] casting, or a transfer-molding machine, and the hardened material of this invention can be obtained by heating at further 80-200 degrees C in 2 - 10 hours.

[0041] Moreover, the epoxy resin constituent of this invention can be dissolved in solvents, such as toluene, a xylene, an acetone, a methyl ethyl ketone, and methyl isobutyl ketone, heat press forming of the prepreg which base materials, such as a glass fiber, carbon fiber, polyester fiber, a polyamide fiber, an alumina fiber, and paper, were infiltrated, and carried out stoving to them and which was obtained to them can be carried out, and a hardened material can also be obtained. The amount which occupies 15 - 65 % of the weight preferably is usually used for the solvent in this case ten to 70% of the weight in the epoxy resin constituent of this invention, and the mixture of this solvent.

[0042] In this way, since the hardened material of this invention obtained is excellent in thermal resistance, a water resisting property, and mechanical strength, it can be used in the extensive field as which thermal resistance, a water resisting property, and high mechanical strength are required. Specifically, it is useful as all electrical and electric equipment and electronic ingredients, such as a closure ingredient, a laminate, and an

insulating material. Moreover, it can use also for fields, such as a molding ingredient, adhesives, composite material, and a coating.

[0043]

[Example] Next, although an example explains this invention still more concretely, it is the weight section unless the section has a notice especially in below. In addition, the Measuring condition of a GPC analysis apparatus, water absorption, and an Izod impact test value is as follows.

[0044]

GPC analysis apparatus Liquid-sending pump: L-6000 (Hitachi make)

UV detector: L-4000 (Hitachi make)

It measures with the absorbance of 254nm. Column: KF-803(1)+KF-802.5 (2)
+ KF-802 (1) (Showa Denko make)

Solvent: Tetrahydrofuran (THF)

Water absorption Test piece (hardened material): Diameter of 50mm 3mm in thickness

Disk The weight rate of increase after boiling by underwater [100-degree C] for 24 hours (%)

Izod impact test value (KJ/m²)

JIS It measures based on K-6911. [0045] It is the following formula (4) to the flask furnished with example 1 thermometer, a dropping funnel, a cooling pipe, a fractionating column, and a stirrer.

[0046]

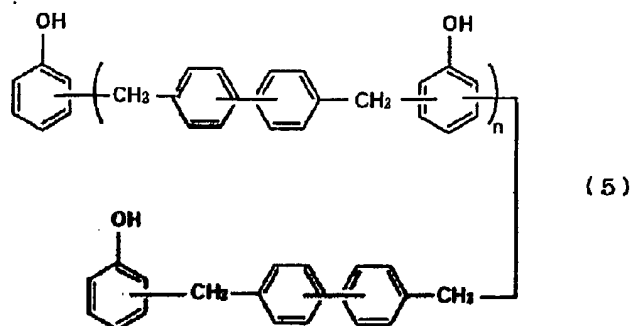
[Formula 6]



[0047] It came out and the compound 107 section and the phenol 113 section which are expressed were taught, and the churning dissolution was carried out under the room temperature, blowing nitrogen. Noticing the p-toluenesulfonic-acid (one hydrate) 0.5 section about generation of heat, it added slowly so that solution temperature might not exceed 50 degrees C. It heats to 120 degrees C in an oil bath after that, and after extracting the water generated using a fractionating column, it was made to react at 120 more degrees C for 5 hours. After reaction termination, methyl-isobutyl-ketone 500ml was added further, and it moved to the separating funnel and rinsed. A solvent is removed from the organic layer after rinsing to a scale loss draft until wash water shows neutrality, and it is the following type (5).

[0048]

[Formula 7]



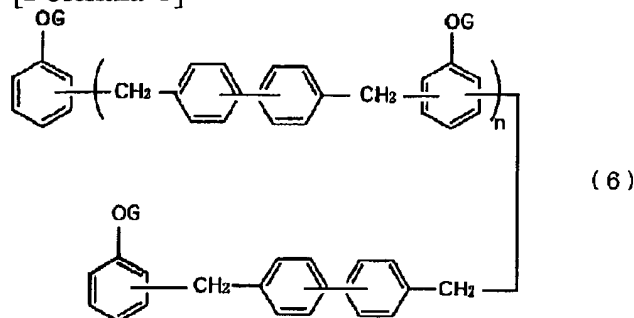
[0049] (-- the inside n of a formula expresses an integer.) -- the novolac mold (resin A) of this invention 156 section expressed was obtained. The percentage of the thing of $n=0$ according [a hydroxyl equivalent] to 203 g/eq and GPC according [the softening temperature of the obtained novolac mold resin] to 85.3 degrees C was 23% in area %.

[0050] Giving a nitrogen gas purge to the flask furnished with example 2 thermometer, a cooling pipe, and a stirrer, the novolac mold (resin A) 102 section obtained in the example 1, the epichlorohydrin 185 section, and the dimethyl sulfoxide 46 section were taught, and it was made to dissolve. It heats at 45 more degrees C, and division addition was carried out over 90 minutes, and the flake-like sodium-hydroxide (99% of pure parts) 20.2 section was made to react at 70 degrees C by 45 more degrees C after that for 1 hour for 2 hours. After reaction termination, it heated at 130 degrees C and the bottom dimethyl sulfoxide of reduced pressure and epichlorohydrin were distilled off, and the methyl isobutyl ketone of the 259 sections was added to the residue, and it dissolved in it.

[0051] Furthermore, rinsing was repeated after heating the solution of this methyl isobutyl ketone at 70 degrees C, adding 30% of the weight of the sodium-hydroxide water-solution 5 section and making it react for 1 hour until pH of a penetrant remover became neutrality. Furthermore, a water layer carries out separation removal, distills scale loss pressing-down methyl isobutyl ketone out of an oil reservoir using a rotary evaporator, and is the following formula (6).

[0052]

[Formula 8]



[0053] (-- n expresses an integer among a formula and G expresses a glycidyl group.) -- the epoxy resin (B)123 section of this invention expressed was obtained. The percentage of the thing of $n=0$ according [weight per epoxy equivalent] to 277 g/eq and GPC according [the softening temperature of the obtained epoxy resin] to 70.5 degrees C was 19% in area %.

[0054] The novolak mold (resin C) 143 section which reacts like an example 1 and is expressed with said formula (5) was obtained except having made the amount of the phenol used into the 141 sections in example 3 example 1. The percentage of the thing of $n=0$ according [softening temperature] to 75.5 degrees C and GPC according [the hydroxyl equivalent of the obtained novolak mold epoxy resin] to 198 g/eq was 41% in area %.

[0055] The epoxy resin (D) 122 section of this invention which performs an epoxidation reaction like an example 2 and is expressed with said formula (6) was obtained except having used the novolak mold (resin C) 99 section obtained in the example 4 example 3. The percentage of the thing of $n=0$ according [weight per epoxy equivalent] to 271 g/eq and GPC according [the softening temperature of the obtained epoxy resin] to 66.7 degrees C was 35% in area %.

[0056] The epoxy resin obtained with the five to example 7 above (B), (D) -- receiving -- as a curing agent -- a phenol novolak (a hydroxyl equivalent -- 106 g/eq) It blends by the presentation shown in the column of a presentation of the compound of Table 1, using triphenyl phosphine (TPP) as 80.3 degrees C of softening temperatures, novolak mold resin (A), and a hardening accelerator. It kneads with a roll at 70 degrees C for 15 minutes, and they are 150 degrees C and the compacting pressure of 50kg/cm². It transfer-molded for 180 seconds, and you made it harden at 180 more degrees C by 160 degrees C after that for 8 hours for 2 hours, the test piece was created, and water absorption and an Izod impact test value were measured. A result is shown in the column of the physical properties of the hardened material of Table 1. Moreover, the numeric value of the column of a presentation of front Naka and a compound shows the weight section.

[0057]

[Table 1]

Table 1 An example 5 Example 6 Presentation of example 7 compound Epoxy resin (B) 100 100 Epoxy resin (D) 100 Phenol novolak 38 39 Novolak mold resin (A) 73 TPP(s) 11 1 Physical properties of a hardened material Water absorption (%) 0.81 0.82 0.65 an Izod impact test value (KJ/m²) -- 27.3 26.5 28.7 [0058]

[Effect of the Invention] The novolak mold resin and the epoxy resin of this invention can give the hardened material excellent in a water resisting property and mechanical strength, and are very useful for wide range applications, such as a molding material, a casting ingredient, a charge of a laminated wood, a coating, adhesives, and a resist.

[Translation done.]

* NOTICES *

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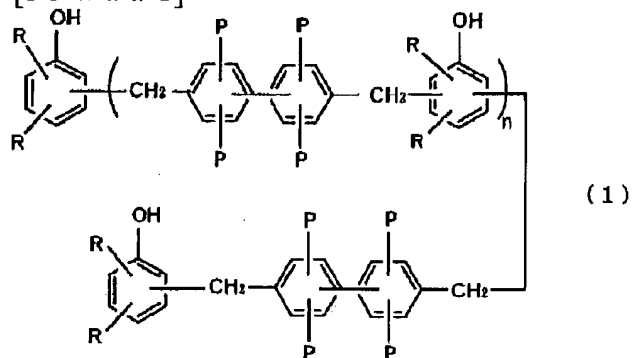
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
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CLAIMS

[Claim(s)]

[Claim 1] Formula (1)

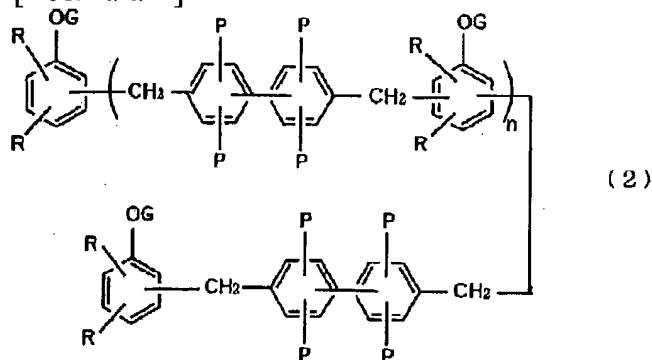
[Formula 1]



(Among a formula (1), n shows the average and takes the value of 0-10.) P and R express either a hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-8 or an aryl group, respectively, and even if each P and R are mutually the same, they may differ. Novolak mold resin whose percentage of the thing [in / on GPC (gel permeation chromatography) analysis and / a formula (1)] of n= 0 it is novolak mold resin expressed and is 70% or less in surface ratio.

[Claim 2] Formula (2)

[Formula 2]



(n, P, and R express the semantics same in a formula (1) among a formula (2).) Moreover, G expresses a glycidyl group. Epoxy resin whose percentage of the thing [in / on GPC analysis and / a formula (2)] of n= 0 it is the epoxy resin expressed and is 70% or less in surface ratio.

[Claim 3] (a) Epoxy resin (b) Epoxy resin constituent which comes to contain novolak mold resin according to claim 1.

[Claim 4] (a) The epoxy resin constituent which comes to contain an epoxy resin (b) curing agent according to claim 2.

[Claim 5] (a) Epoxy resin (b) according to claim 2 Epoxy resin constituent which comes to contain novolak mold resin according to claim 1.

[Claim 6] An epoxy resin constituent given in any 1 term of claims 3, 4, or 5 containing a hardening accelerator.

[Claim 7] An epoxy resin constituent given in any 1 term of claims 3, 4, 5, or 6 containing an inorganic filler.

[Claim 8] The hardened material which comes to harden the epoxy resin constituent of a publication in any 1 term of claims 3, 4, 5, 6, or 7.

[Translation done.]

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(54) 【発明の名称】 ノボラック型樹脂、エポキシ樹脂、エポキシ樹脂組成物及びその硬化物

(57) 【要約】

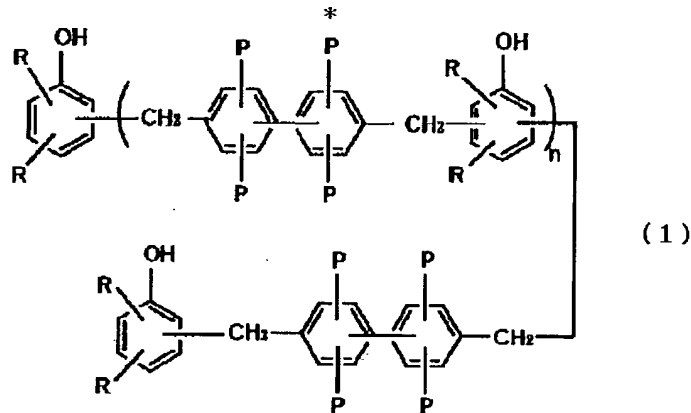
【課題】耐水性、及び靱性に優れた硬化物を与え、作業性に優れたノボラック型樹脂及びエポキシ樹脂を提供すること。

【解決手段】ビフェニル化合物とフェノール類を縮合することにより得られるノボラック型樹脂及び該ノボラック型樹脂をグリシジルエーテル化することにより得られるエポキシ樹脂であって、GPCチャートによる低分子量の分子の割合が面積比で70%以下であるノボラック型樹脂及びエポキシ樹脂。

【特許請求の範囲】

【請求項1】式(1)

*【化1】

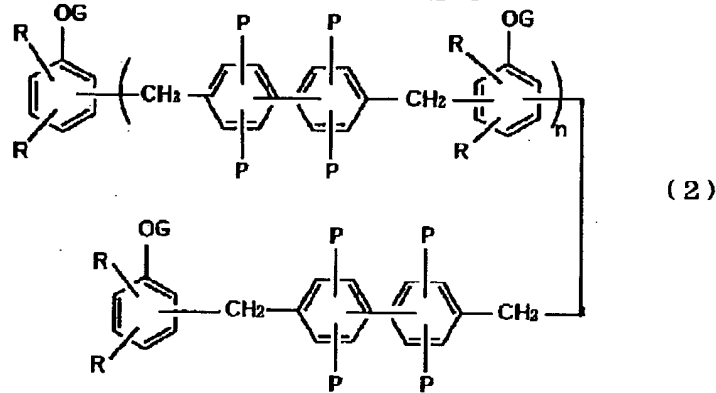


(式(1)中、nは平均値を示し0~10の値を取る。
P、Rはそれぞれ水素原子、ハロゲン原子、炭素数1~8のアルキル基、またはアリール基のいずれかを表し、個々のP、Rは互いに同一であっても異なってもよい。)で表されるノボラック型樹脂であって、GPC ※

※(ゲルパーミエーションクロマトグラフィー)分析において式(1)におけるn=0のものの割合が面積比で70%以下であるノボラック型樹脂。

【請求項2】式(2)

【化2】



(式(2)中、n、P、Rは式(1)におけるのと同じ意味を表す。またGはグリシジル基を表す。)で表されるエポキシ樹脂であって、GPC分析において式(2)におけるn=0のものの割合が面積比で70%以下であるエポキシ樹脂。

【請求項3】(a) エポキシ樹脂

(b) 請求項1記載のノボラック型樹脂

を含有してなるエポキシ樹脂組成物。

【請求項4】(a) 請求項2記載のエポキシ樹脂

(b) 硬化剤

を含有してなるエポキシ樹脂組成物。

【請求項5】(a) 請求項2記載のエポキシ樹脂

(b) 請求項1記載のノボラック型樹脂

を含有してなるエポキシ樹脂組成物。

【請求項6】硬化促進剤を含有する請求項3、4または5のいずれか1項に記載のエポキシ樹脂組成物。

【請求項7】無機充填材を含有する請求項3、4、5または6のいずれか1項に記載のエポキシ樹脂組成物。

【請求項8】請求項3、4、5、6または7のいずれか★50

★1項に記載のエポキシ樹脂組成物を硬化してなる硬化物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は耐水性、機械的強度に優れる硬化物を与えるノボラック型樹脂、エポキシ樹脂およびエポキシ樹脂組成物に関する。

【0002】

40 【従来の技術】エポキシ樹脂は種々の硬化剤で硬化させることにより、一般的に機械的性質、耐水性、耐薬品性、耐熱性、電気的性質などの優れた硬化物となり、接着剤、塗料、積層板、成形材料、注型材料などの幅広い分野に利用されている。従来、工業的に最も使用されているエポキシ樹脂としてビスフェノールAにエピクロヒドリンを反応させて得られる液状および固形のビスフェノールA型エポキシ樹脂がある。その他液状のビスフェノールA型エポキシ樹脂にテトラブロムビスフェノールAを反応させて得られる難燃性固形エポキシ樹脂などが汎用エポキシ樹脂として工業的に使用されている。

【0003】

【発明が解決しようとする課題】しかしながら、前記したような汎用エポキシ樹脂は分子量が大きくなるにつれて、それを硬化して得られる硬化物の韌性は増加するものの耐熱性が低下するという欠点がある。また、耐熱性の低下を補うためにクレゾールノボラックエポキシ樹脂などの多官能エポキシ樹脂を混合した場合に得られる硬化物は耐熱性は高くなるものの、韌性は低下し吸水率は高くなるという欠点がある。一方、最近の電子産業などの目ざましい発達に伴い、これらに使用される電気絶縁材料などに要求される耐水性及び機械強度（韌性）は益々厳しくなっており、これらの特性に優れた硬化剤及びエポキシ樹脂の出現が待ち望まれている。

【0004】このような要求を満たすエポキシ樹脂及びその硬化剤の例として特開平5-117350号にビフェニルフェノール骨格を持ったノボラック型樹脂（硬化剤）及びエポキシ樹脂が例示されている。しかし、このような構造のノボラック型樹脂の場合、樹脂中に含ま*

*れる低分子量の分子の割合が高いと、得られた樹脂は融点の高い結晶となる傾向がある。ノボラック型樹脂が融点の高い結晶となった場合、精製後反応器からの取り出しが困難になるという問題がある。またエポキシ樹脂の硬化剤として使用するには、混練時の温度を非常に高くしなければならない必要性が生じ、作業性に支障を来す恐れがある。

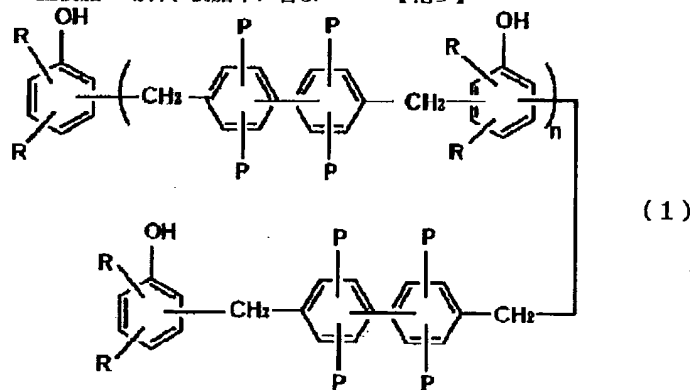
【0005】

【課題を解決するための手段】本発明者らはこうした実状に鑑み、耐水性及び機械強度に優れた硬化物を与え、しかも作業性に優れた硬化剤及びエポキシ樹脂を求めて鋭意研究した結果、特定の分子構造及び分子量分布を有するノボラック型樹脂及びエポキシ樹脂が、前記の特性を満たすものであることを見出して本発明を完成させるに至った。

【0006】すなわち本発明は式（1）

【0007】

【化3】



(1)

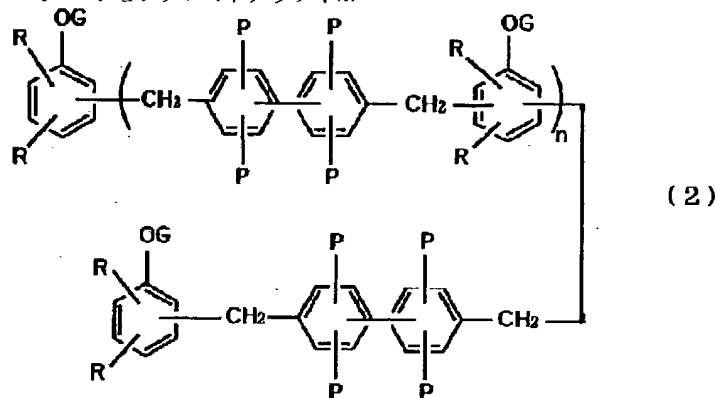
【0008】（式（1）中、nは平均値を示し0～10の値を取る。P、Rはそれぞれ水素原子、ハロゲン原子、炭素数1～8のアルキル基、またはアリール基のいずれかを表し、個々のP、Rは互いに同一であっても異なってもよい。）で表されるノボラック型樹脂であって、GPC（ゲルパーミエーションクロマトグラフィ※

※一）分析において式（1）におけるn=0のものの割合が面積比で70%以下であるノボラック型樹脂、

（2）式（2）

【0009】

【化4】



(2)

【0010】（式（2）中、n、P、Rは式（1）におけるのと同じ意味を表す。またGはグリシジル基を表す。）で表されるエポキシ樹脂であって、GPC分析において式（2）におけるn=0のものの割合が面積比で

★50

70%以下であるエポキシ樹脂。

【0011】(3)(a)エポキシ樹脂

(b)上記(1)記載のノボラック型樹脂

を含有してなるエポキシ樹脂組成物、

(4)(a)上記(2)記載のエポキシ樹脂

(b)硬化剤

を含有してなるエポキシ樹脂組成物、

(5)(a)上記(2)記載のエポキシ樹脂

(b)上記(1)記載のノボラック型樹脂

を含有してなるエポキシ樹脂組成物、

(6)硬化促進剤を含有する上記(3)、(4)または

(5)のいずれか1項に記載のエポキシ樹脂組成物、

(7)無機充填材を含有する上記(3)、(4)、

(5)または(6)のいずれか1項に記載のエポキシ樹脂組成物、

(8)上記(3)、(4)、(5)、(6)または

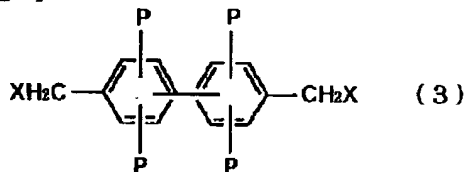
(7)のいずれか1項に記載のエポキシ樹脂組成物を硬化してなる硬化物を提供する。

【0012】

【発明の実施の形態】式(1)で表される化合物は例え 20
ば式(3)

【0013】

【化5】



【0014】(式中、Xはハロゲン原子、水酸基、低級 30
アルコキシ基を表す。Pは式(1)におけるのと同じ意味を表す。)

【0015】で表される化合物とフェノール類とを酸触媒の存在下で縮合反応させることにより得ることができる。

【0016】式(2)で表される化合物は例えば、式(1)で表される化合物とエビハロヒドリンとの反応をアルカリ金属水酸化物の存在下で行うことにより得ることができる。

【0017】式(3)においてハロゲン原子としては塩 40
素原子、臭素原子が、また、低級アルコキシ基としてはメトキシ基、エトキシ基などがそれぞれ好ましい具体例として挙げられる。

【0018】ここで式(1)の化合物を得るために用い 50
うるフェノール類の具体例としては、フェノール、クレゾール、エチルフェノール、n-プロピルフェノール、イソブチルフェノール、t-ブチルフェノール、オクチルフェノール、ノニルフェノール、キシレノール、メチルブチルフェノール、ジ-tert-ブチルフェノール等の各種o-、m-、p-異性体、またはシクロペンチルフェ

ノール、シクロヘキシルフェノール、シクロヘキシルクレゾール等のシクロアルキルフェノール、またはフェニルフェノール等の置換フェノール、またはモノプロモフェノール、ジプロモフェノール等のハロゲン化フェノール類が挙げられる。これらのフェノール類は1種類のみを用いてもよく、2種類以上を組み合わせて用いてもよい。

【0019】上記縮合反応を行う場合、フェノール類の使用量は式(3)で表される化合物1モルに対して通常 1.1~10モル、好ましくは1.2~8モル、特に好ましくは1.2~5モルである。フェノール類の使用量が多い場合、残存フェノール類を留去する際、得られた縮合物が高融点の結晶となり、濃縮器から取り出せなくなる恐れがある。この結晶化の問題を防ぐために効果的な縮合物の分子量分布は式(1)におけるn=0のものの割合がGPCを用いて分子量分布を測定した場合の総面積に対する面積割合が70%以下のものであり、好ましくは65%以下のものである。

【0020】上記縮合反応においては酸触媒を用いる。酸触媒としては種々のものが使用できるが塩酸、硫酸、p-トルエンスルホン酸、シュウ酸等の無機あるいは有機酸、三弗化ホウ素、無水塩化アルミニウム、塩化亜鉛などのルイス酸が好ましく、特にp-トルエンスルホン酸、硫酸、塩酸が好ましい。これら酸触媒の使用量は特に限定されるものではないが、通常式(3)で表される化合物の0.1~30重量%用いる。

【0021】上記縮合反応は無溶剤下で、あるいは有機溶剤の存在下で行うことができる。用いうる有機溶剤の具体例としては、メチルセロソルブ、エチルセロソルブ、トルエン、キシレン、メチルイソブチルケトンなどが挙げられる。有機溶剤の使用量は仕込んだ原料の総重量に対して通常50~300重量%、好ましくは100~250重量%である。反応温度は通常40~180℃、反応時間は通常1~10時間である。これらの溶剤類は単独で、あるいは数種類を混合して用いることが出来る。また、反応中に生成する水或はアルコール類などを系外に分留管などを用いて留去することは、反応を速やかに行う上で好ましい。

【0022】反応終了後、洗浄液のpH値が3~7、好ましくは5~7になるまで水洗処理を行う。水洗処理を行う場合は必要により水酸化ナトリウム、水酸化カリウムなどのアルカリ金属水酸化物、水酸化カルシウム、水酸化マグネシウムなどのアルカリ土類金属水酸化物、アンモニア、リン酸二水素ナトリウムさらにはジエチレントリアミン、トリエチレンテトラミン、アニリン、フェニレンジアミンなどの有機アミンなど様々な塩基性物質等を中和剤として用いてもよい。また水洗処理は常法にしたがって行えばよい。例えば反応混合物中に上記中和剤を溶解した水を加え分液抽出操作をくり返す。

【0023】中和処理を行った後、減圧加熱下で溶剤及

び未反応物を留去し生成物の濃縮を行い、式(1)で表

される本発明のノボラック型樹脂を得ることが出来る。

【0024】式(1)で表される化合物から本発明のエポキシ樹脂を得る方法としては公知の方法が採用できる。例えば前記で得られた式(1)で表される化合物と過剰のエピクロロヒドリン、エピプロムヒドリン等のエピハロヒドリンの溶解混合物に水酸化ナトリウム、水酸化カリウム等のアルカリ金属水酸化物を添加し、または添加しながら20~120℃の温度で1~10時間反応させることにより本発明のエポキシ樹脂を得ることが出来る。

【0025】本発明のエポキシ樹脂を得る反応において、アルカリ金属水酸化物はその水溶液を使用してもよく、その場合は該アルカリ金属水酸化物の水溶液を連続的に反応系内に添加すると共に減圧下、または常圧下連続的に水及びエピハロヒドリンを留出させ、更に分液し水は除去しエピハロヒドリンは反応系内に連続的に戻す方法でもよい。

【0026】また、式(1)で表される化合物とエピハロヒドリンの溶解混合物にテトラメチルアンモニウムクロライド、テトラメチルアンモニウムブロマイド、トリメチルベンジルアンモニウムクロライド等の4級アンモニウム塩を触媒として添加し50~150℃で1~5時間反応させて得られる式(1)の化合物のハロヒドリンエーテル化合物にアルカリ金属水酸化物の固体または水溶液を加え、20~120℃で1~10時間反応させ脱ハロゲン化水素(閉環)させる方法でもよい。この場合使用される4級アンモニウム塩の量は、式(1)の化合物中の水酸基1個に対して、通常1~10gであり、好ましくは2~8gである。

【0027】これらの反応において使用されるエピハロヒドリンの量は式(1)で表される化合物の水酸基1当量に対し通常1~20モル、好ましくは2~10モルである。アルカリ金属水酸化物の使用量は式(1)で表される化合物の水酸基1当量に対し通常0.8~1.5モル、好ましくは0.9~1.1モルである。更に、反応を円滑に進行させるためにメタノール、エタノールなどのアルコール類の他、ジメチルスルホン、ジメチルスルホキシド等の非プロトン性極性溶媒などを添加して反応を行うことが好ましい。

【0028】アルコール類を使用する場合、その使用量はエピハロヒドリンの量に対し通常2~20重量%、好ましくは4~15重量%である。また非プロトン性極性溶媒を用いる場合はエピハロヒドリンの量に対し通常5~100重量%、好ましくは10~90重量%である。

【0029】これらのエポキシ化反応の反応物を水洗後、または水洗無しに加熱減圧下、110~250℃、圧力10mmHg以下でエピハロヒドリンや溶媒などを除去する。また更に加水分解性ハロゲンの少ないエポキシ樹脂とするために、得られたエポキシ樹脂をトルエ

ン、メチルイソブチルケトンなどの溶剤に溶解し、水酸化ナトリウム、水酸化カリウムなどのアルカリ金属水酸化物の水溶液を加えて更に反応を行い閉環を確実にものにすることもできる。この場合アルカリ金属水酸化物の使用量はエポキシ化に使用した式(1)の化合物の水酸基1当量に対して通常0.01~0.3モル、好ましくは0.05~0.2モルである。反応温度は通常50~120℃、反応時間は通常0.5~2時間である。

【0030】反応終了後、生成した塩をろ過、水洗などにより除去し、更に、加熱減圧下トルエン、メチルイソブチルケトンなどの溶剤を留去することにより本発明のエポキシ樹脂が得られる。

【0031】以下、本発明のエポキシ樹脂組成物について説明する。前記(3)、(5)、(6)、(7)記載のエポキシ樹脂組成物において本発明のノボラック型樹脂はエポキシ樹脂の硬化剤として作用し、この場合本発明のノボラック型樹脂を単独または他の硬化剤と併用することが出来る。併用する場合、本発明のノボラック型樹脂の全硬化剤中に占める割合は30重量%以上が好ましく、特に40重量%以上が好ましい。

【0032】本発明のノボラック型樹脂と併用される他の硬化剤としては、例えばアミン系化合物、酸無水物系化合物、アミド系化合物、フェノール系化合物などが挙げられる。用いうる硬化剤の具体例としては、ジアミノジフェニルメタン、ジエチレントリアミン、トリエチレンテトラミン、ジアミノジフェニルスルホン、イソホロンジアミン、ジシアンジアミド、リノレン酸の2量体とエチレンジアミンとより合成されるポリアミド樹脂、無水フタル酸、無水トリメリット酸、無水ピロメリット酸、無水マレイン酸、テトラヒドロ無水フタル酸、メチルテトラヒドロ無水フタル酸、無水メチルナジック酸、ヘキサヒドロ無水フタル酸、メチルヘキサヒドロ無水フタル酸、フェノールノボラック、及びこれらの変性物、イミダゾール、BF₃・アミン錯体、グアニジン誘導体などが挙げられるが、エポキシ樹脂の硬化剤として公知のものであればこれらに特に限定されない。これら硬化剤は単独で用いてもよく、2種以上併用してもよい。

【0033】前記(4)、(5)、(6)、(7)記載のエポキシ樹脂組成物において本発明のエポキシ樹脂は単独または他のエポキシ樹脂と併用して使用することが出来る。併用する場合、本発明のエポキシ樹脂の全エポキシ樹脂中に占める割合は30重量%以上が好ましく、特に40重量%以上が好ましい。

【0034】本発明のエポキシ樹脂と併用されうる他のエポキシ樹脂の具体例としてはノボラック型エポキシ樹脂、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、ビフェニル型エポキシ樹脂などが挙げられるが、これらは単独で用いてもよく、2種以上併用してもよい。

【0035】前記(3)、(6)、(7)のエポキシ樹

脂組成物において、硬化剤として本発明のノボラック型樹脂を用いる場合、エポキシ樹脂としては前記の他のエポキシ樹脂や本発明のエポキシ樹脂を用いることが出来る。

【0036】また前記(4)、(6)、(7)のエポキシ樹脂組成物において、エポキシ樹脂として本発明のエポキシ樹脂を用いる場合、硬化剤としては前記の他の硬化剤や本発明のノボラック型樹脂を用いることが出来る。

【0037】本発明のエポキシ樹脂組成物において硬化剤の使用量は、エポキシ樹脂のエポキシ基1当量に対して0.7~1.2当量が好ましい。エポキシ基1当量に対して、0.7当量に満たない場合、あるいは1.2当量を超える場合、いずれも硬化が不完全となり良好な硬化物性が得られない恐れがある。

【0038】また上記硬化剤を用いる際に硬化促進剤を併用しても差し支えない。用いうる硬化促進剤の具体例としては例えば2-メチルイミダゾール、2-エチルイミダゾール、2-エチル-4-メチルイミダゾール等のイミダゾール類、2-(ジメチルアミノメチル)フェノール、1,8-ジアザビシクロ(5,4,0)ウンデセン-7等の第3級アミン類、トリフェニルホスフィン等のホスフィン類、オクチル酸スズなどの金属化合物などが挙げられる。硬化促進剤はエポキシ樹脂100重量部に対して0.1~5.0重量部が必要に応じ用いられる。

【0039】本発明のエポキシ樹脂組成物は、必要により無機充填材を含有する。用いうる無機充填材の具体例としては、シリカ、アルミナ、タルク等が挙げられる。無機充填材は、本発明のエポキシ樹脂組成物中において0~90重量%を占める量が必要に応じ用いられる。さらに本発明のエポキシ樹脂組成物には、シランカップリング剤、ステアリン酸、パルミチン酸、ステアリン酸亜鉛、ステアリン酸カルシウム等の離型剤、顔料等種々の配合剤を添加することができる。

GPC分析装置

送液ポンプ：L-6000(日立製作所製)

UVディテクター：L-4000(日立製作所製)

254nmの吸光度で測定

カラム：KF-803(1本)+KF-802.5(2本)

+KF-802(1本) (昭和電工製)

溶媒：テトラヒドロフラン(THF)

吸水率

試験片(硬化物)：直径50mm

厚さ3mm 円盤

100℃の水中で24時間煮沸した後の重量増加率(%)

アイゾット衝撃試験値(KJ/m²)

JIS K-6911に準拠し測定

【0045】実施例1

温度計、滴下ロート、冷却管、分留管、攪拌器を取り付※50

※けたフラスコに、下記式(4)

【0046】

*【0040】本発明のエポキシ樹脂組成物は、各成分を所定の割合で均一に混合することにより得られる。本発明のエポキシ樹脂組成物は従来知られている方法と同様の方法で容易にその硬化物とすることができる。例えば本発明のエポキシ樹脂と硬化剤、必要により硬化促進剤及び無機充填材並びに種々の配合剤とを必要に応じて押出機、ニーダ、ロール等を用いて均一になるまで充分に混合して本発明のエポキシ樹脂組成物を得、そのエポキシ樹脂組成物を溶融後注型あるいはトランスファー成形機などを用いて成形し、さらに80~200℃で2~10時間に加熱することにより本発明の硬化物を得ることができる。

【0041】また本発明のエポキシ樹脂組成物をトルエン、キシレン、アセトン、メチルエチルケトン、メチルイソブチルケトン等の溶剤に溶解させ、ガラス繊維、カーボン繊維、ポリエステル繊維、ポリアミド繊維、アルミナ繊維、紙などの基材に含浸させ加熱乾燥して得たブリアレグを熱プレス成形して硬化物を得ることもできる。この際の溶剤は、本発明のエポキシ樹脂組成物と該溶剤の混合物中で通常10~70重量%、好ましくは15~65重量%を占める量を用いる。

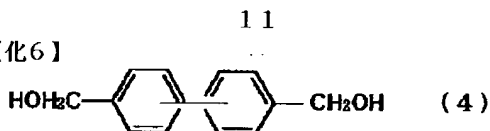
【0042】こうして得られる本発明の硬化物は耐熱性、耐水性及び機械強度に優れているため、耐熱性、耐水性、高機械強度の要求される広範な分野で用いることができる。具体的には封止材料、積層板、絶縁材料などのあらゆる電気・電子材料として有用である。また、成型材料、接着剤、複合材料、塗料などの分野にも用いることができる。

【0043】

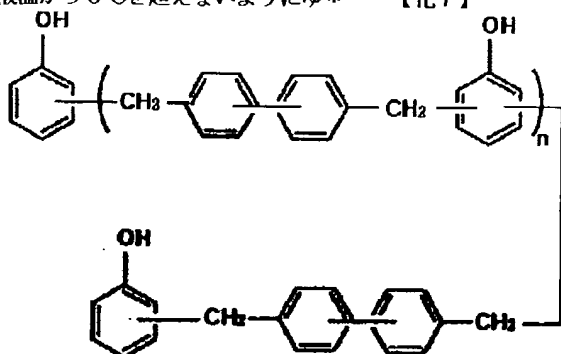
【実施例】次に本発明を実施例により更に具体的に説明するが、以下において部は特に断わりのない限り重量部である。なお、GPC分析装置、吸水率、アイゾット衝撃試験値の測定条件は次の通りである。

【0044】

【化6】



【0047】で表される化合物107部、フェノール113部を仕込み、室温下、窒素を吹き込みながら攪拌溶解した。p-トルエンスルホン酸（1水和物）0.5部を発熱に注意しながら液温が50℃を超えないようにゆ*



【0049】（式中nは整数を表す。）で表される本発明のノボラック型樹脂（A）156部を得た。得られたノボラック型樹脂の軟化点は85.3℃、水酸基当量は203 g/e q、GPCによるn=0のものの割合は面積%で23%であった。

【0050】実施例2

温度計、冷却管、攪拌器を取り付けたフラスコに窒素ガスバージを施しながら実施例1で得られたノボラック型樹脂（A）102部、エピクロルヒドリン185部、ジメチルスルホキシド46部を仕込み溶解させた。更に45℃に加熱しフレーク状水酸化ナトリウム（純分99%）20.2部を90分かけて分割添加し、その後更に※

1 2
* たっぷり添加した。その後油浴中で120℃まで加熱し、分留管を用いて生成する水を抜き出した後、更に120℃で5時間反応させた。反応終了後、更にメチルイソブチルケトン500mlを加え、分液ロートに移し水洗した。洗浄水が中性を示すまで水洗後有機層から溶媒を加熱減圧下に除去し、下記式（5）

【0048】

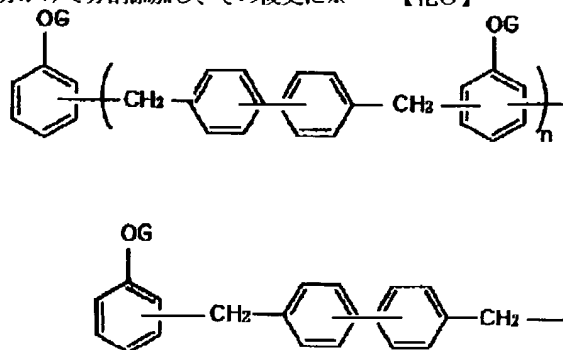
【化7】

20※45℃で2時間、70℃で1時間反応させた。反応終了後、130℃に加熱し減圧下ジメチルスルホキシド及びエピクロルヒドリンを留去し、残留物に259部のメチルイソブチルケトンを加え溶解した。

【0051】更にこのメチルイソブチルケトンの溶液を70℃に加熱し30重量%の水酸化ナトリウム水溶液5部を添加し1時間反応させた後、洗浄液のpHが中性となるまで水洗を繰り返した。更に水層は分離除去し、ロータリエバポレーターを使用して油層から加熱減圧下メチルイソブチルケトンを留去し、下記式（6）

【0052】

【化8】



【0053】（式中、nは整数を表し、Gはグリシジル基を表す。）で表される本発明のエポキシ樹脂（B）123部を得た。得られたエポキシ樹脂の軟化点は70.5℃、エポキシ当量は277 g/e q、GPCによるn=0のものの割合は面積%で19%であった。

【0054】実施例3

実施例1においてフェノールの使用量を141部にした以外は実施例1と同様に反応を行い前記式（5）で表さ★50

★れるノボラック型樹脂（C）143部を得た。得られたノボラック型エポキシ樹脂の水酸基当量は198 g/e q、軟化点は75.5℃、GPCによるn=0のものの割合は面積%で41%であった。

【0055】実施例4

実施例3で得られたノボラック型樹脂（C）99部を用いた以外は実施例2と同様にエポキシ化反応を行い前記式（6）で表される本発明のエポキシ樹脂（D）122

13

部を得た。得られたエポキシ樹脂の軟化点は66.7℃、エポキシ当量は271g/eq、GPCによる $n=0$ のものの割合は面積%で35%であった。

【0056】実施例5～7

前記で得られたエポキシ樹脂(B)、(D)に対し、硬化剤としてフェノールノボラック(水酸基当量106g/eq、軟化点80.3℃)及びノボラック型樹脂(A)、硬化促進剤としてトリフェニルホスフィン(TPP)を用い、表1の配合物の組成の欄に示す組成で配*

配合物の組成

エポキシ樹脂(B)

エポキシ樹脂(D)

フェノールノボラック

ノボラック型樹脂(A)

TPP

硬化物の物性

吸水率(%)

アイゾット衝撃試験値(KJ/m²)

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*合して、70℃で15分ロールで混練し、150℃、成形圧力50kg/cm²で180秒間トランスファー成形して、その後160℃で2時間、更に180℃で8時間硬化せしめて試験片を作成し、吸水率、アイゾット衝撃試験値を測定した。結果を表1の硬化物の物性の欄に示す。また、表中、配合物の組成の欄の数値は重量部を示す。

【0057】

【表1】

表1

実施例5	実施例6	実施例7
100		100
	100	
38	39	
		73
1	1	1
0.81	0.82	0.65
27.3	26.5	28.7

【0058】

【発明の効果】本発明のノボラック型樹脂及びエポキシ樹脂は耐水性及び機械強度に優れた硬化物を与えること※

※ができ、成形材料、注型材料、積層材料、塗料、接着剤、レジストなど広範囲の用途にきわめて有用である。